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Water Rock Interaction [WRI 14]**Raman spectroscopy of adsorbed water in clays: first attempt at band assignment****Dominique de Ligny^{a*}, Emmanuel Guillaud^a, H       Gailhanou^b, Philippe Blanc^b**^a*Institut Lumi  re Mati  re, CNRS, Universit   Lyon 1, 12 rue Ada Byron, 69622 Villeurbanne, France*^b*BRGM, Service D3E, 3 avenue Claude Guillemin, 45000 Orl      , France*

Abstract

Raman spectroscopy can be a useful tool to determine water content within clays, or even in highly saturated solutions. The following assignment is proposed for the OH region of SAz-2: the two large bands at 3260 and 3475 cm⁻¹ are assigned to water in pores, the first one to water molecules coordinated to the interlayer cations, and the second one to structural Al-OH groups. The band at 3600 cm⁻¹ is therefore more likely related to adsorbed water on the clay surface. Simple intensity ratios of these different bands give good estimates of water content.

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1. Introduction

Water in clays is a key issue for geology as well as material sciences. Indeed departure of adsorbed water from clays in sedimentary basin probably regulates the smectite to illite transition. It then plays a key role in reservoir formation as well as petroleum maturation. In the industrial side, especially in waste management, clays are used as active barrier that tend to prevent spreading of toxic elements in the environment. Water availability and its diffusion within the clay are here essential to understand how such barriers can be efficient.

Structure of water in clays is difficult to study for many aspects. First, it evolves rapidly with water partial pressure. Secondly usual techniques of structure determination as X-ray are not sensitive to hydrogen position. Vibrational spectroscopies are therefore used in the frequency range of OH bond

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vibrations around 3500 cm^{-1} . Mainly infra-red spectroscopy (IR) and NMR were used until now [1-3]. Raman spectroscopy is a vibrational spectroscopy complementary to IR but with different selection rules more restrictive and therefore presenting sharper vibration band than IR. Even very sensitive to luminescence, Raman spectroscopy was rarely used to study hydrous minerals because often such emissions mask the Raman spectra. Using a UV laser as excitation source we were able to overcome this last restriction and to present here a first set of data on a smectite sample.

Water is present in clays in a variety of form. First it is a constitutive of the mineral itself, and OH groups can be found in the octahedral sheets. It can be also present in three different ways inside clays: in pores, adsorbed on clay surfaces or between layers, especially around exchangeable cations. All these OH groups contribute to the vibrational bands around 3500 cm^{-1} . The first goal of this paper is to give some keys to constrain OH band assignment, preliminary to any later understanding of OH structure in clays. A study of OH in highly saturated salt solution is also presented as a possible analogous of the hydration sphere around the interlayer cation.

2. Materials and methods

The sample studied is the SAz-2 from the Clay Mineral Society. It is from Cheto Arizona. The structural formula taken from [4] is $(\text{Ca}_{.39}\text{Na}_{.36}\text{K}_{.02})[\text{Al}_{2.71}\text{Mg}_{1.11}\text{Fe(III)}_{.12}\text{Mn}_{.01}\text{Ti}_{.03}][\text{Si}_{8.00}]\text{O}_{20}(\text{OH})_4$. The interlayer cation is therefore mainly calcium with an interlayer charge of -1.08. The sample was only dispersed in distilled water and equilibrated at different relative humidity using saturated solution of various salts [5] or dried in air.

In order to see the effect of cation solvation by water, solutions were prepared by dissolving weighted NaOH crystals in 4ml of distilled water. The concentrations of this set of solutions range from 2 to 50 wt.% by 4 wt.% steps.

A micro-spectrometer Raman Horiba Jobin Yvon® LabRAM Aramis was used to collect the spectra. To prevent luminescence a laser UV HeCd by Kimmon® at 325 nm was used in association with a 2400 l/cm grating. Nevertheless some luminescence was still present from time to time. Its effect was removed by baseline subtraction in the 2750 to 3900 cm^{-1} range using a polynomial function of degree 5 with the labspec software. This data reduction has no effect on band frequency position.

3. Results and discussion

3.1. Clay versus free water

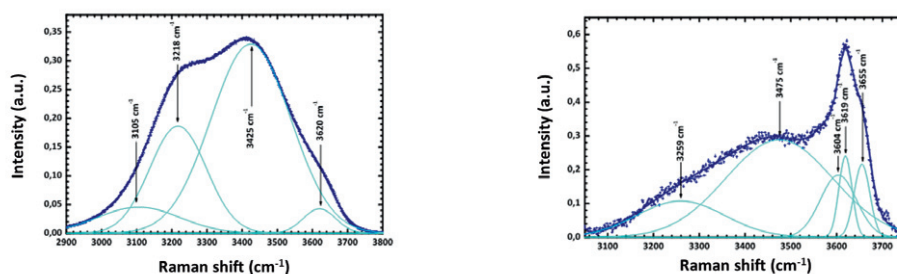


Fig. 1. Raman spectra of (a) liquid water and (b)SAz-2. The position of the Gaussian fit is reported on the graphs.

In Figure 1 we compare the spectra obtained on free water and on SAz-2. In order to identify the different bands, the curve fitting of the Raman spectra by several Gaussian curves is shown. The number of bands in liquid water changes depending of the authors. A deconvolution in four bands, in agreement with [6], was used because it reproduces well the global spectra with the fewer contributions. The band at 3218 cm^{-1} is assigned to symmetrical stretching of the OH bond inside a tetra-coordinated structure, and the band at 3425 cm^{-1} to the asymmetric one [6]. The two other bands are not yet consensually assigned.

In the clay the two lower bands are roughly at the same frequency than liquid water and they correspond to water molecule in a tetra-coordinated arrangement probably in pore structures. The three narrower high frequency bands are intrinsic to the clay. In muscovite a unique contribution at 3660 cm^{-1} is assigned unambiguously to hydroxyl group linked to Al octahedra. However, IR measurements show Fe-OH at 3604 cm^{-1} and Al-OH or Mg-OH around 3619 cm^{-1} [3,7]. To overcome this ambiguity measurements have been performed on solutions saturated in NaOH.

3.2. O-H vibration in highly saturated solution

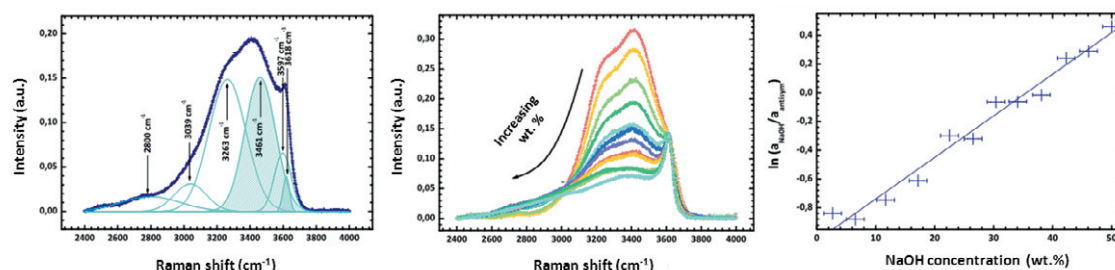


Fig. 2. (a) Raman spectra for the NaOH solution at 17.2 wt.%. (b) Evolution of the Raman spectra for increasing concentration of NaOH, the spectra are normalized at 3618 cm^{-1} . (c) Intensity ratio between the intensity at 3618 cm^{-1} (OH associated with sodium cation) and at 3461 cm^{-1} (antisymmetric stretching of pure water) versus the NaOH concentration.

In the interlayer domain water is often considered to form hydration sphere around the charge compensator cation [8-9]. This structure therefore should not be very far from cation concentrated solutions. In figure 2, the effect of the concentration in a NaOH solution is shown. It can be clearly recognized the two main bands of water which decrease quickly when cation concentration evolves. At high frequency two sharp peaks are present at 3597 and 3618 cm^{-1} and can be assigned to the interaction between OH and sodium cation. Even if free water had a band at 3620 cm^{-1} , the band width in NaOH is much narrower making the two contributions very distinct. This is confirmed by the very good correlation presented in fig. 2c. In the future this correlation could be used to measure the chemical concentration of water by Raman spectroscopy.

At very high concentration new bands appear at lower frequency and were assigned to H_3O_2^+ due to OH^- transformation [10]. No such bands were ever observed in clays even at very low Relative Humidity since no pH variation is taking place in the interlayer.

3.3. Evolution with the Relative Humidity

Concerning the evolution of interlayer water with relative humidity, two approaches were investigated. One consisted in a direct drying of a drop of clay suspension and therefore recording the spectra evolution with time (Fig 3 a-b). The second consisted to equilibrate the clay with different saturated salt solutions (Fig 3 c). In both cases using the area ratio between the free water contribution below 3535 cm^{-1} and the total area of the OH region, a good evaluation of the water content was possible. At very low Relative

Humidity the only contribution still present is that one at 3660 cm^{-1} . Since no more removable water is present in the sample, this last band can be assigned to vibration of Al-OH and Mg-OH groups inside the octahedral layer in agreement with muscovite data.

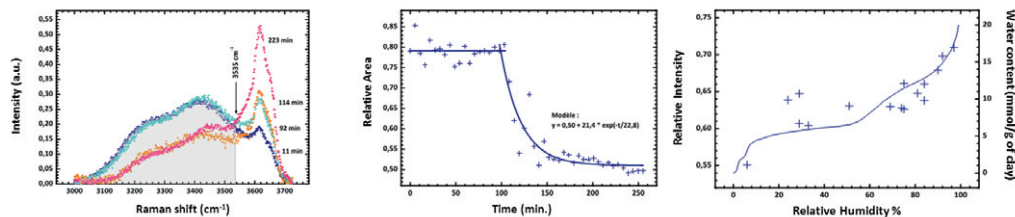


Fig. 3. Evolution of the Raman spectra in the OH region with the relative humidity.

4. Conclusion

The following assignment is proposed for the OH region of SAz-2: the two large bands at 3260 cm^{-1} and 3475 cm^{-1} are assigned to water in pores, and the band at 3620 cm^{-1} to water molecules coordinated to the interlayer cations. The band at 3600 cm^{-1} is therefore more likely connected to adsorbed water on the clay surface.

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